PVDF Based Polymer-Ceramic Nanocomposites for Capacitive Energy Storage Applications

Thesis submitted in the partial fulfillment for the Award of Degree

Doctor of Philosophy

By

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Year 2024

Chapter-VI

Summary and Future Scope

6.1 Summary

In this present thesis, we have investigated and explained the potential of non-conducting fillers/matrix in PVDF-based nanocomposites for capacitive energy storage applications and studied the mechanism behind the improvement of dielectric properties with introduction of ceramics in the PVDF polymer. In chapter III, we have used ceramic nanoparticles as a matrix and PVDF polymer as filler while in chapter IV and V, ceramic nanoparticles have been reinforced in PVDF polymer matrix to enhance the dielectric and energy storage properties of the developed composites. We have fabricated PVDF-based flexible capacitors with ceramic fillers and achieved increased dielectric constant, high polarization and improved dielectric breakdown strength with non-degraded mechanical properties allowing the film to withstand very high electric field. The developed composites have higher value of energy storage density that is attributed to the significantly enhanced polarization of the nanocomposite films, improved dielectric properties and breakdown strength. We have shown that ceramic nanoparticles play a crucial role in enhancing the performance of nanocomposites and flexibility is maintained which allows their applications in flexible electronics.

The main aim of this research work was to synthesize and study PVDF polymer-based nanocomposites with non-conducting ceramics which are lead free with high dielectric constant, high dielectric breakdown strength, large polarization, low dielectric loss and low manufacturing cost. The primary goal was to enhance dielectric properties for capacitive energy storage applications. Our research focused on the development of high-performance and cost-effective PVDF-based nanocomposite dielectric films for capacitive energy storage with an emphasis on understanding the underlying mechanisms and optimizing the synthesis process. We also tried to optimize the synthesis conditions for PVDF nanocomposite dielectric films.

The major outcomes of our current research work are as follows:

1. $Ba_{0.7}Sr_{0.3}TiO_3$ – PVDF (Polyvinylidene fluoride) ceramic-polymer composites have been synthesized using a cold sintering process. $Ba_{0.7}Sr_{0.3}TiO_3$ (BST) nanoparticles were synthesized using sol-gel combustion method. The BST nanoparticles were used for synthesizing the $Ba_{0.7}Sr_{0.3}TiO_3$/PVDF composite with 80 wt.% BST and 20 wt. % PVDF. X-ray diffraction analysis confirmed pure phase formation of BST and revealed presence of different polar phases of PVDF in certain conditions. XRD pattern confirmed the formation of pure perovskite phase of BST with cubic structure having Pm-3m space group. In case of hot pressed BST/PVDF composite, crystallization of β phase and in case of annealed BST/PVDF composite, crystallization of γ-phase dominates. Thermal stability and surface morphology of the composites have been studied using thermo-gravimetric analysis and SEM respectively. TGA/DSC analysis revealed that composite is stable for the applications up to 300 ºC. Dielectric and ferroelectric properties have been studied. Thermally stable dielectric constant and dielectric loss has been obtained from room temperature to 200 ºC in case of annealed BST/PVDF composites. Polarization-Electric field hysteresis loop analysis of composite reveals that significantly higher dielectric breakdown strength (more than 400 kV/cm) have been achieved in comparison to pure ceramic which is the main requirement for a potential material in energy storage applications. Discharge efficiency of BST/PVDF annealed composite upto 95 % and high thermal stability up to 300 ºC has been achieved in case of BST/PVDF annealed composite which is big achievement for a ceramic matrix composite with polymer filler.

2. $BaZrO_3$ (BZ)/PVDF (Polyvinylidene difluoride) Polymer nanocomposites have been synthesized for energy storage applications using solution casting method. Barium zirconate (BZ) has been synthesized by using high energy ball mill method and BZ/PVDF ceramic nanocomposites have been synthesized in thin film form using 90 wt. % PVDF polymers as a matrix and 10 wt.% BZ as nanofillers. XRD analysis has been performed to check successful synthesis of nanocomposites. We have synthesized pure PVDF film, BZ/PVDF and hy-BZ/PVDF composite film and have achieved value of dielectric constant for the hy-BZ/PVDF composite film ($\varepsilon_r \sim 26$) almost three times of the value of dielectric constant for pure PVDF film. FTIR spectra of hy-BZ powder have shown the successful hydroxylation of $BaZrO_3$ filler. TGA curve shows that there is no observed weight loss upto 450^0C in case of composites. Polarization has also been increased upto almost double in case of hy-BZ/PVDF composite in comparison to pure PVDF film. We have achieved energy storage density of 1.11 J/cm^3 for hy-BZ/PVDF composite much higher than the pure PVDF which is equal to 0.47 J/cm^3. The dielectric breakdown strength has also been analysed using Weibull analysis technique and obtained to be 1495 kV/cm in case of hy-BZ/PVDF composites.
3. We have synthesized $BaZr_{0.4}Ti_{0.6}O_3$ (BZT) ceramic nanoparticles using nano milling process and hy-BZT/PVDF composite film using solution casting method with 10 wt. % of BZT nanoparticle as filler and 90 wt. % of PVDF polymer as a matrix. XRD pattern of composites confirm the successful formation of composites. FTIR spectra confirmed the successful hydroxylation of BZT powder for better dispersion. Differential scanning calorimetry analysis indicated improved degree of crystallinity in case of composites. The dominance of polar

phase of PVDF in composites was observed due to interfacial interaction among filler nanoparticles. The significantly enhanced dielectric permittivity ($\varepsilon_r \sim 25.5$) and ferroelectric properties have been obtained in case of hy-BZT/PVDF composite film in comparison to pure PVDF film ($\varepsilon_r \sim 8$). The value of dielectric breakdown strength for hy-BZT/PVDF composite has been calculated using Weibull analysis and found to be 1754 kV/cm. We have calculated energy storage density for hy-BZT/PVDF composite and found it to be 0.41 J/cm^3 at electric field of 790 kV/cm. The above synthesized composites may be a suitable replacement of existing materials with improved dielectric properties for energy storage applications.

In short, introduction of ceramic has enhanced the dielectric constant and energy storage properties of PVDF based composites. The enhancement in dielectric and polarization responses of composites with the ceramic filler/matrix is due to transformation of PVDF from nonpolar phase to polar phase and space charge polarization at the interfaces. The phase transformations in PVDF have been confirmed from XRD analysis and FTIR spectroscopy. The improvement in the value of electric polarization is observed due to Maxwell-Wagner interfacial polarization.

6.2 Future scope

Basically, present thesis work has been performed to improve the dielectric and energy storage properties of PVDF based polymer ceramic nanocomposites which resulted in development of many high energy density nanocomposites. In chapter III, PVDF polymer-based nanocomposites have been synthesized in pellet form using PVDF as a filler and ceramic as a matrix with the help of recently invented cold sintering process at extraordinary low temperature. In chapter IV and V, PVDF based nanocomposites have been synthesized using solution casting method in film form which is budget friendly. More advanced synthesis methods such as spin coating, electrospinning might be explored to produce even thinner films, enabling higher applied electrical fields during P-E hysteresis loop testing.

Future scopes in this research area are as follows:

- ❖ Different other suitable ceramics with different shapes and sizes can be selected to synthesize PVDF polymer based ceramic nanocomposites using polymer as a matrix and ceramic as a nanofiller.
- ❖ Microstructural analysis and polymer ceramic interface effect can be studied in more detail for PVDF based nanocomposites using PVDF polymer as a filler and ceramic as a matrix synthesized by cold sintering process.
- ❖ Different coupling agents can be applied on specific ceramic nanofiller to reinforce in PVDF polymer matrix to get the idea of best coupling agent for that specific nanofiller so that the dielectric and energy storage properties of PVDF based polymer composites having such fillers could be maximized. The comparative study using different coupling agents can also be performed.
- ❖ Investigations can be performed on the role of space charge polarization in the enhancement of dielectric constants and energy storage density. Advanced techniques, such as pulsed electroacoustic methods or thermally stimulated depolarization current measurements can be employed to get a deep understanding of the contributions of space charge polarization.
- ❖ Theoretical techniques and simulations can also be employed to gain insights into the behavior of fillers and their compatibility within different matrices. Molecular dynamics simulations, density functional theory calculations, and finite element

analysis can provide valuable insights into the compatibility of fillers with the matrix and can guide in the design of superior nanocomposites.

With adoption of these suggestions into future work, the overall understanding of the dielectric and energy storage properties may be enhanced and potentially lead to the development of advanced materials with superior energy storage density.